

Downstream Details



Hot Off the Press!

This United States Department of Energy, **National Petroleum Technology Office (NPTO)** newsletter is the first edition of a semi-annual newsletter highlighting the projects funded through the **Emerging Processing Technology Applications (EPTA)** program. The goals of the program are to: 1) develop cleaner and more efficient refining technologies; and 2) develop transportation fuels that reduce air pollution.

The projects funded through the EPTA program address the following issues:

- Production of ultra-clean petroleum fuels from domestic and imported crude and from alternative hydrocarbon feedstocks (natural gas, petroleum coke, refinery bottoms, coal, waste materials, biomass) that are equal to or better than current petroleum fuels
- Development of fuel/engine combinations that meet future (and more restrictive) vehicle emission standards
- Development of refining catalysts with improved selectivities, yields, and lifetimes
- Increased refinery plant and process reliability
- Improved energy efficiency of refining processes and equipment
- Improved separation technologies
- Development of new approaches to upgrading and refining heavy feeds regulations

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The first edition of **Downstream Details** was created by **Shawn A. Trivette**, a summer student intern at the NPTO Tulsa, OK, during summer 2000. Shawn is a Junior at Tennessee Technological University majoring in Chemical Engineering. The DOE summer intern program provides learning opportunities at Department of Energy facilities and is implemented by the Oak Ridge Associated Universities in Oak Ridge, TN.



Metal Oxides Could Help Lower Sulfur in Cat-Cracked Gasoline

The U.S. Environmental Protection Agency (EPA) has mandated that by the year 2003, the sulfur content in gasoline be less than 30 ppm.



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Make your plans now

As such, much of the current research in oil refining is concentrating on lowering the sulfur content of gasoline. **Idaho National Engineering and Environmental Laboratory (INEEL)** has begun a project that will focus on producing low-sulfur catalyst-cracked (cat-cracked) gasoline by intercepting the hydrogen sulfide (H₂S) used in cat cracking. The premise of this work is that many sulfur compounds from cat-cracked gasoline are formed during the cracking process by reaction of crude oil compounds with H₂S.

The main problem with sulfur is that it oxidizes in the engine, poisoning the catalytic converters in automobiles. When these converters are poisoned, they become less activated and increased levels of nitrogen oxides are discharged from the tailpipe. This means an increase in emission of the NO_x pollutants and unburned hydrocarbons.

The yield of straight-run gasoline obtained by simple crude distillation is insufficient to meet the U.S. demand for gasoline. Therefore conversion of larger, heavier molecules to those in gasoline's boiling range requires Fluid Catalytic Cracking (FCC). This technology is the main process for converting heavy ends to gasoline and is reported as being a major source of 98% of the sulfur in gasoline. This means either that lowering the sulfur content of gasoline will require lowering the sulfur content of feed to the FCC or post-treating of FCC products to meet sulfur specifications.

The approach taken will be to conduct FCC reactions in a small-scale laboratory unit. The main methods to prevent the formation of sulfur compounds will involve intercepting the H₂S, typically by its reaction with metal oxides or sulfur dioxide (SO₂), as shown in **Figure 1**. A metal oxide used in conjunction with the FCC catalyst would be converted to the sulfide by reaction with H₂S and then recovered during regeneration of the FCC catalyst. The Claus reaction (equation II) also is an attractive reac-

tion mechanism because sulfur dioxide is available from the catalyst generator.

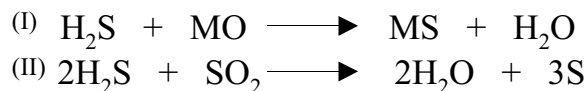


Figure 1: Desulfurization methods.

The apparatus to be used is modeled after a microconfined bed unit (MCBU) with a fluidized catalyst bed. Mass and sulfur balances will be obtained and the concentration of sulfur compounds in the gasoline boiling range will be determined using gas chromatography with a sulfur selective detector. Gas chromatography and mass spectrometry will be used to identify predominant sulfur compounds. Work is expected to be completed by mid-2001.

For more information, contact the INEEL contract project manager, Dr. Ray Anderson at 208-526-1623 or e-mail him at anderp@inel.gov. **DD**

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DownstreamDetails is a biannual newsletter devoted to providing information about DOE's Emerging Processing Technology Applications Projects. For more information on these projects, contact **Kathy Stirling**, Project Manager, DOE's National Petroleum Technology Office:

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Bacteria Remove Sulfur from Heavy Crude Oils

SO₂ emissions from the combustion of transportation fuels are an environmental concern. Crude oils being refined are becoming heavier and contain more sulfur. In order to keep the sulfur and its related compounds from being released into the environment, refiners are looking for inexpensive ways to remove sulfur from the fuels they market. A 1995-98 collaborative effort between **Oak Ridge National Labs (ORNL)** and several industries was designed to explore and develop bioprocessing alternatives for desulfurization. This research was headed by Dr. Abhijeet Borole. The project looked at biodesulfurization by three strains of microorganisms.

Biodesulfurization was analyzed using an emulsion phase contactor (EPC) and a batch stirred reactor (BSR). The EPC is shown in **Figure 2**. Similar biodesulfurization studies from 1999 and 2000 have recently been completed by Idaho National Engineering and Environmental Laboratory (INEEL), with research headed by Dr. Ray Anderson, and **Brookhaven National Laboratories (BNL)**, with research headed by Mow Lin. Industry involvement was included with both laboratories' work.

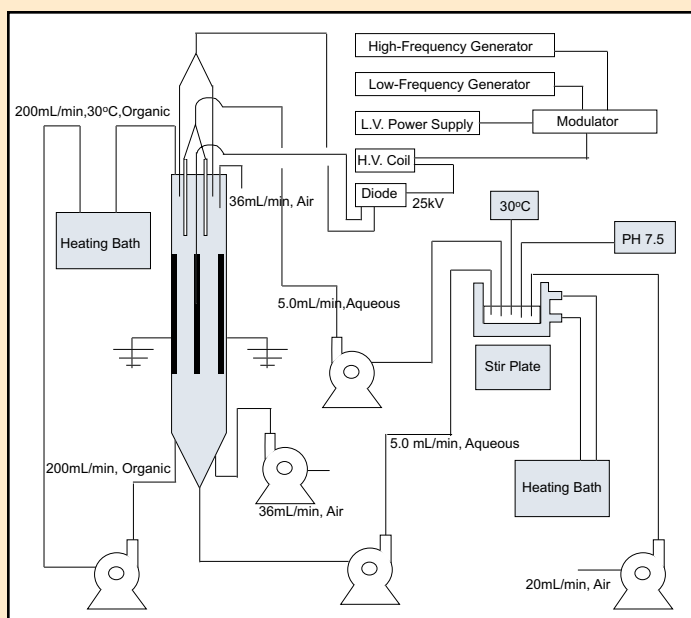


Figure 2: Schematic of emulsion phase contactor and equipment used by ORNL.

INITIAL ORNL EXPERIMENTS

Dibenzothiophene (DBT), a common sulfur compound in crude, was used as the model compound in these tests of biodesulfurization of crude oils (see **Figure 3**). Early stages of the project were devoted to reductive biocatalyst development, but lacking promise for desulfurizing DBT, efforts were re-focused on aerobic microbes to produce biocatalysts. Tests were done on impeller rates and cell density for the biocatalysts involved. These tests showed that the desulfurization process is controlled mostly by kinetics of the biochemical reaction and is limited at higher cell densities by how quickly the biocatalyst can reach the reaction interface.

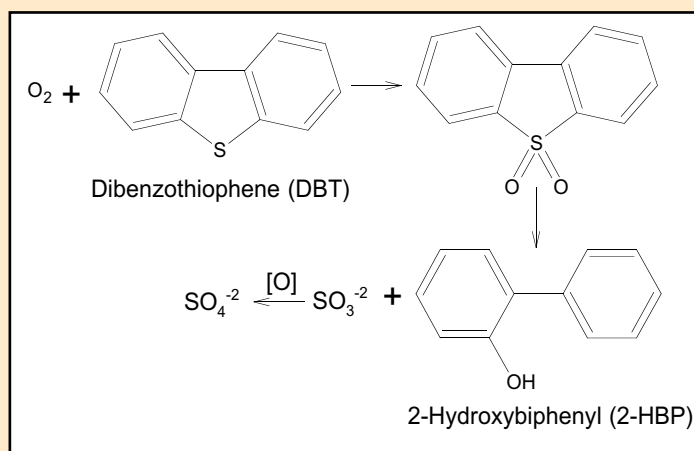


Figure 3: Desulfurization of dibenzothiophen (DBT).

It was initially assumed that greater desulfurization would be found using the EPC setup rather than the BSR. However, effectiveness of EPC was similar to BSR, suggesting that EPC did not provide a larger surface area for reaction under the pretest conditions. This would imply that a simpler, standing bioreactor would be just as effective with these biocatalysts as a more complex, and more expensive, EPC.

CRUDE OIL EXPERIMENTS


After the tests on a controlled reactant were completed, the biocatalysts were tested on actual crude

oils. The experiments in the EPC indicated that it may not be necessary to spray the crude oil with the biocatalyst for the duration of the period required for reaction. Emulsion holdup was such that after a few hours of spraying, the desulfurization reaction continued. This shows that it may be sufficient to spray at the outset and follow with minimal mixing steps until the end of the reaction time, thereby saving money by using less biocatalyst.

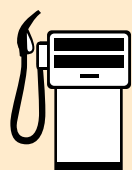
Overall, it was found that certain biocatalysts can remove sulfur efficiently from DBT and substituted DBTs. However, though the biocatalysts can affect many of the organosulfur compounds in crude oils, there are still many sulfur compounds that they cannot desulfurize. Currently, Dr. Anderson of INEEL is investigating biocatalysis in critical fluid systems. A critical fluid is a material heated above the temperature at which compression does not cause condensa-

tion. Though focused on sulfur compounds, it is expected that other beneficial transformations such as viscosity reductions can occur. These experiments are focusing on biocatalytic transformation of organosulfur compounds and development of critical fluid reactors.

Dr. Anderson found that DBT solubility in supercritical CO₂ is 5,000 times greater than in water, and solubility can be varied by adjusting temperature and pressure. Similar increases in solubility are expected for other organic sulfur compounds found in crude oil.

For more information, contact Dr. Abhijeet P. Borole at ORNL by calling 865-576-7421 or e-mailing him at borolea@ornl.gov; Dr. Ray Anderson at INEEL by calling 208-526-1623 or e-mail him at anderp@inel.gov; or Dr. Mow Lin at BNL by calling 931-344-3064 or emailing him at mow@bnl.gov. 

Clay Complexes Support HDS Catalyst



Hydroprocessing represents a crucial component of petroleum refining operations both in terms of environmental and economic considerations. Regulations concerning maximum amount of sulfur content of gasoline and emissions of sulfur-oxide compounds upon combustion are becoming more and more stringent.

One 1994-2000 focus of **Argonne National Laboratory (ANL)** has been the development of catalysts for hydrodesulfurization (HDS). Typical HDS catalysts are comprised of Co-Mo sulfides or Ni-Mo sulfides on an alumina support. Modification of the pore structure of the support has generated great attention among researchers.

Most desulfurization test reactions have used dibenzothiophene (DBT) as the model compound to test various configurations of support material with Co-Mo-S and Ni-Mo-S catalysts. In this testing, the desired product would be biphenyl and hydrogen

sulfide (H₂S) (shown in **Figure 4** equation I). A competing reaction creates cyclohexylbenzene by saturating one aromatic ring prior to desulfurization (**Figure 4** equation II). Ring saturation requires more costly hydrogen and is not desirable. Fortunately, a more effective catalyst for adding hydrogen at the sulfur site without hydrogenating the aromatic rings has been found. However, this has only been tested on DBT.

HDS uses various types of catalysts to add hydrogen to reduce unwanted sulfur compounds. Typically this requires expensive, high-pressure, high-temperature equipment to produce the environmentally friendly low-sulfur fuels. ANL scientists identified several new desulfurization catalysts with

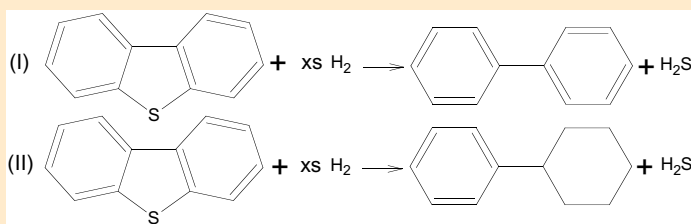


Figure 4: HDS catalysts.


improved HDS activity and selectivity. From these new catalysts, it may be possible to achieve HDS processing at lower temperature and pressure.

The catalysts used for HDS at ANL are various clay complexes. Natural clays have a history of use in the hydroprocessing industry since they are abundant and inexpensive. ANL's approach is to create synthetic organo-clay complexes (SOCC). An advantage of SOCC's is that the pore size and distribution can be controlled by the synthesis method, and the purity of the synthetic clays is high compared to naturally occurring clay minerals. ANL researchers found the best pore sizes for optimum catalyst activity to be in the mesopore range, between 1.8 nm and 10 nm. Mesoporous synthetic clays (MSC) are obtained when silicate gels containing organic compounds are hydrothermally crystallized to form layered clays containing organic polymers. The template (organic polymer) molecules are then removed from the synthetic polymer-clay complex by calcination (burning off the organics), which involves heating the complex to high temperatures in air.

After calcination, the MSC materials were examined as potential supports for HDS. Pore diameter of the MSC catalysts was found to have a strong effect

on both HDS activity and selectivity. Efforts are being made to more efficiently create and control the pore size of clays since pore sizes that are too large (approaching macropores, or greater than 10 nm) lower the catalyst activity. Mesoporous range MSC catalysts are of most interest for HDS of increasingly heavy oils. By changing the molecular weight or loading of the organic polymer used, the clay particles can be propped apart to varying degrees. The material is calcined in air at this point to avoid low porosity and decreased utility of the material. Apparently, the clay particles are locked into the position they were prior to calcination with pores occurring where the organic polymer used to be.

Lower-pressure, lower-temperature desulfurization would be a boon to refiners, since the average HDS unit in the U.S. reaches only 600 psig—well below the pressure required for meeting EPA's new sulfur specifications. Advances in catalyst development can help refiners reduce the initial capital construction cost of revamping, or operating high-pressure and high-temperature HDS units.

For more information, contact Dr. Christopher Marshall at ANL at 630-252-4310 or e-mail him at CLMarshall@anl.gov. 

NPTO Research Provides Data Before EPA Sets Regulations on Small Particle Emissions

Particulate matter (PM) is the term for chemical-ly and physically diverse substances that exist as discrete particles over the size from 0.005-100 micrometers that tend to remain airborne. Gaseous compounds can condense or interact with PM to form larger particles. PM can break off from solid material that initially is too large to remain suspended as these particles are acted upon by physical forces (turbulence or sheering), liquefy (melt), or sublime to a gaseous state.

The **U.S. Environmental Protection Agency (EPA)** is currently considering regulations on airborne particulate matter from engine exhausts that have a mean diameter of less than 2.5 micrometers (referred to as PM_{2.5}). Regulations on PM_{2.5} should be based on the best scientific data for characterization because there may be health risks in inhaling PM of small size. Some scientists believe that PM effects on human health are closely related to particle size distributions and morphology, as well as the valence

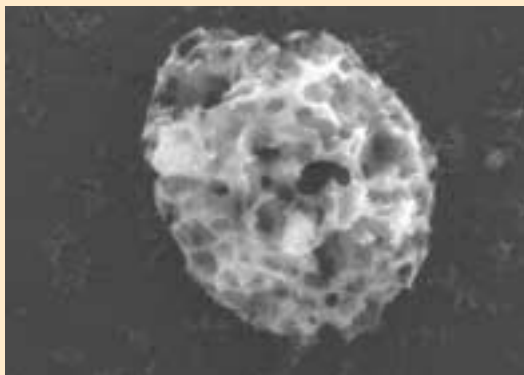


Figure 4: Carbon rich char particles found in exhaust from hydrocarbon exhaust.

and solubility of certain elements in the PM. It is important that PM_{2.5} from various sources be thoroughly characterized in order to identify chemical structural features that may be related to health effects. It is therefore essential to identify and evaluate analytical methods that can provide such structural information. Although there are many analytical techniques for determining the elemental composition of PM_{2.5}, information on molecular structure and microstructure is difficult to obtain.

Two of the primary petroleum sources of PM_{2.5} are combustion of residual fuel oil (home heating oil) and diesel engines. Dr. Gerald Huffman, University of Kentucky, recently began research in ways to identify fine particulate matter found in exhaust of hydrocarbon combustion (**Figure 4**). His main research goals have been to identify sources of PM_{2.5}, characterize mass structures of PM_{2.5}, identify structural features of PM_{2.5}, identify features of PM_{2.5} affecting human health. Particulate samples (collected on teflon and quartz filters) from exhaust from a



Figure 5: Test diesel engine used in University of Kentucky research.

heavy duty diesel engine (**Figure 5**) were supplied by the EPA National Risk Management Research Laboratory in North Carolina. Huffman used thermal desorption gas chromatography and mass spectroscopy (TD GC/MS) to determine composition of the samples, x-ray absorption fine structure (XAFS) spectroscopy to determine sulfur percentages and positions in the molecules, and magnetic susceptibility to measure magnetization dependency on temperature.

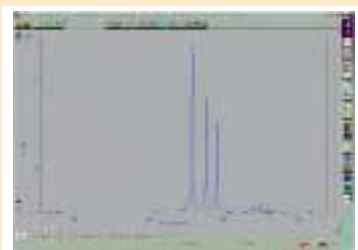
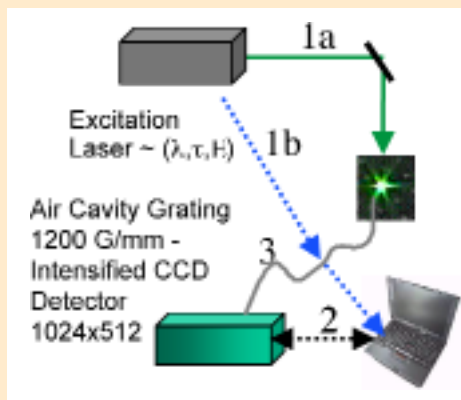
These analytical techniques provide a more complete analysis of the molecular structure of both inorganic and organic components of the PM_{2.5}. Improved information has also been obtained on particle size distributions, composition ranges, and morphologies. Since both health effects and source apportionment of PM_{2.5} may be closely related to such parameters, this type of information should be valuable to regulatory authorities and to industry showing compositions of PM_{2.5} and sulfur levels.

For more information, contact Dr. Gerald Huffman at 606-257-4027 or e-mail him at cffls@pop.uky.edu. **ID**

Real-Time In-Situ Measurements of Elemental Composition in Gases and Aerosols

Several trace metals are known to be toxic to human health and ecosystems. Trace metal emissions from oil-fired and coal combustion are regulated by the U.S. Environmental Protection Agency (EPA).

Continuous emission monitoring of trace metals associated with airborne particulate matter requires techniques that perform the measurement in real time and in situ. Real-time characterization of small



Windows screen display:
Cr-laden aerosol particles.

Figure 6: Time-resolved laser plasma spectroscopy coupled with aerosol focusing provides a high-precision solution for field portable metal measurement.

airborne particles of significance to industrial emissions, environmental air toxins, and human exposure can now be achieved using a technological breakthrough made by **Oak Ridge National Laboratory (ORNL)** researchers.


Dr. Meng-Dawn Cheng employed the principles of time-resolved laser-induced plasma spectroscopy (LIPS) in the design of a portable instrument for real-time, in-situ measurement of elemental composition in gas and aerosol phases. The work involves a novel design that combines subsonic aerosol beam focusing and time-resolved laser-induced plasma techniques (**Figure 6**).

A microplasma is produced by focusing a high-power laser on aerosols to generate plasma. The emission wavelength at a given delay time, with respect to the plasma ignition, reveals the identity of trace elements, and the time-resolved emission intensity provides a means for quantitative determination. The aerosol focusing technique enables the instrument to sample particles and continuously concentrates particle mass through a focal point. Sampling is particle size-selective and real-time size selection can be made by varying the operating conditions. Different contours of the aerosol focusing geometry have been examined and an optimal configuration to couple with the optical measurement has been constructed. A pulsed microplasma is optically generated at the focal point by using a high-power solid-

state laser. Research using synthetic monodispersed aerosol standards of controlled particle size and chemistry reveals that in-situ laser plasma spectrometry for aerosol samples can be possible only with the use of the aerosol focusing technique.

The field-portable, miniaturized LIPS monitor can provide high-precision continuous measurement of the elemental composition for an aerosol with virtually no sample preparation and with minimal sample contamination. Aerosol particles in the range of a few nanometers to a few micrometers in diameter have been measured.

Savings in cost and time associated with sample analysis can be significant. The ability to provide real-time, in-situ data can be a valuable tool for a wide variety of applications. Detailed experimental and theoretical investigations produced a data set that improves the fundamental understanding of aerosol-laser interaction. This patent-pending technique was field tested during the summer of 2000 through a Cooperative Research and Development Agreement (CRADA) under negotiation with Tennessee Eastman Chemicals.

For more information contact Dr. Meng-Dawn Cheng at 865-241-5918 or e-mail him at **cheng-md@ornl.gov**. 



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CALENDAR

Meetings

November 9-10, 2000

National Petrochemical and Refiners Association

2000 Lubricants & Waxes Meeting
Omni Houston Hotel
Houston, TX
Phone: (202) 457-0480
Yvette_Brooks@npradc.org

November 12-17, 2000

American Institute of Chemical Engineers

2000 Annual Meeting
Los Angeles, CA

Phone: (212) 591-7338

Fax: (212) 591-8894

E-mail: meetmail@aiche.org

December 6-8, 2000

American Chemical Society

Regional Meeting-
Southeast/Southwest
New Orleans, LA
Office of Regional Meetings
Phone: 1-800-227-5558
E-mail: reglmtgs@acs.org

December 14-19, 2000

American Chemical Society

Pacifichem 2000,
Honolulu, Hawaii
E-mail: pacifichem@acs.org
Fax: (202) 872-6128

March 18-20, 2001

National Petrochemical and Refiners Association (NPRA)

Annual Meeting
New Orleans, LA
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